Saltwater Intrusion Releases Iron and Phosphorus from Agricultural Soils

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Abstract: Saltwater intrusion (SWI) associated with global sea-level rise pervasively occur in agricultural lands, with potential to alter biogeochemical cycles and reduce agricultural yields. As SWI encroaches on coastal areas, agricultural fields can release large quantities of phosphorus (P) into nearby waterways due to interactions between sulfate (SO_4^{2-}) and iron (Fe), that make Fe less available to sequester P. This study investigates key biogeochemical mechanisms that mediate the interaction between saltwater, Fe and P in coastal agricultural soils. We collected agricultural soil on the Lower Eastern Shore of Maryland and exposed it to eight different salt treatments under aerobic and anaerobic conditions over a period of thirty days. We analyzed the PO_4^{3-} and Fe concentration in soil-water and total Fe in treated soil at days 0, 15, and 30. The results show that soil-water Fe and PO_4^{3-} concentrations increase under anaerobic conditions over time in all eight salt treatments, suggesting that SWI can stimulate Fe and PO_4^{3-} release under anaerobic conditions despite variation in saltwater compositions. The high levels of PO_4^{3-} in sodium (Na)-containing treatments indicate that increases in sodicity can facilitate P release; the high levels of Fe in treatments consisting $CaSO_4$ show that the presence of Ca potentially prompts the interaction between Fe and SO_4^{2-}.

Introduction

As sea-level rises due to climate change, ocean water moves to inland freshwater areas above and belowground through tidal surges, storms, and groundwater. This phenomenon is called saltwater intrusion (SWI), which can potentially alter biogeochemical cycles in agricultural soils and reduce crop yields. Extensive agricultural areas in the Chesapeake Bay region will be lost by 2050 due to SWI (Shepard et al. 2013). With centuries of farming and fertilizer inputs, agriculture contributes 40% of nitrogen (N) and 46% phosphorus (P) loading into the Chesapeake Bay region (Sharpley et al. 2014). The SWI can cause agricultural soils transition to wetland habitat and potentially cause a large outflux of nutrients from soils (Jordan et al., 2018). This process can promote dead zones and eutrophication (Jordan et al., 2018), resulting in a loss of ecosystem services such as healthy fisheries and waterfowl populations (Boesch, 2016). Thus, a better understanding of the nutrient cycling in agricultural lands should be developed to improve water quality in the Bay and its tributaries.

The objective of this study is to investigate the impact of saltwater intrusion on P and Fe release in agricultural soils on the Lower Eastern Shore of Maryland. One key reason for the nutrient release is that oxidized iron (Fe) becomes less available to stabilize phosphorus (P) in saline sediments (Ann et al. 2000; Hartzell et al. 2010; Patrick et al. 1974), as shown in Figure 1. In soil, PO_4^{3-} couples tightly with ferric forms of iron (Fe(III) complexes). Under the influence of saltwater intrusion, Fe(III) can be reduced to Fe(II). Consequently, both Fe(II) and PO_4^{3-} are released in dissolved form in the water column.

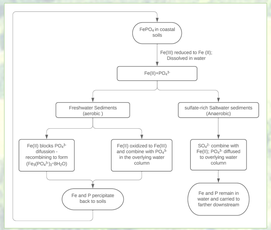

Figure 1. Iron-Phosphate Underlying Mechanism Diagram

We hypothesized that the increase in concentrations of seawater SO_4^{2-} combined with high levels of Fe in soil stimulates the release of P into soil water. We also hypothesized P release will be greater in soils in SO_4^{2-} rich water under anaerobic conditions than that under aerobic conditions. Furthermore, the underlying biogeochemical mechanism that mediates the interaction between saltwater and Fe was explored in this study to assist in understanding the effect of large-scale saltwater intrusion on coastal agricultural soils.

Materials and Methods

Soil Collection and Treatment

We collected soils from an active agricultural land in the Chesapeake Bay Region. Soils were exposed to the following treatment in solutions: 1) Na_2SO_4 where the SO_4^{2-} at fifteen part per thousand (ppt); 2) $CaSO_4$ (15 ppt of SO_4^{2-}); 3) NaCl (15 ppt of Cl^-); 4) NaCl + Na_2SO_4 (15 ppt of SO_4^{2-}); 5) NaCl + $CaSO_4$ (15 ppt of SO_4^{2-} + Cl^-); 6) NaCl + Na_2SO_4 + $CaSO_4$ (15 ppt of SO_4^{2-} + Cl^-); 7) Instant Ocean (15ppt of SO_4^{2-} + Cl^-) and; 8) Deionized water only (freshwater control). Each treatment was replicated four times, and the entire experiment was run under aerobic and anaerobic conditions. 17 mL of the soil-water sample was collected three times over a period of thirty days (t = 0, 15, 30). Samples were analyzed for bioavailable P on a Lachat Quikchem 8500 Flow Injection Analyzer (Hach, Loveland, Co).

Hydroxylamine Iron Extraction

- adapted from the ferrozine method described in Viollier et al. (Viollier et al. 2000)
- The reducing agent, 1.4 mol/L hydroxylamine hydrochloride prepared in a solution of 2 mol/L hydrochloric acid.
- The buffer solution, 10 mol/L ammonium acetate solution adjusted to pH 9.5 with a solution of ammonium hydroxide
- 1.034 mL reducing agent was added to 5 mL and allowed to react for 10 minutes
- 0.345 mL buffer solution was added and allowed to stay for 2 hours

DCB extraction

- uses a powerful reductant, dithionite, to reduce Fe(III) oxides to Fe(II)
- Citrate-bicarbonate solution: mix volume ratio 4:1 of 0.3M sodium citrate: 1M sodium bicarbonate
- 0.8g of dry and treated soil + 0.8g of sodium dithionite + 40mL of the citrate-bicarbonate solution
- Shake at high speed for 16 hours, then centrifuged for 20 minutes at 600RPM

Oxalate extraction

- Oxalate method dissolved the poorly crystalline forms of iron in soils
- Oxalate-oxalic acid solution: mixing volume ratio 4:3 of 0.2M ammonium oxalate : 0.2M oxalic acid. The pH was adjusted to 3 using ammonium oxalate or oxalic acid
- 0.4 g of dry and treated soil + 40 mL of the oxalate-oxalic acid solution + cover with tin foils
- Shake at high speed for 4 hours, then centrifuged for 15 minutes at 600RPM

**All decant supernatant from extraction was filtered and analyzed for iron concentration on the PinAAcle 900T Atomic Absorption

Results

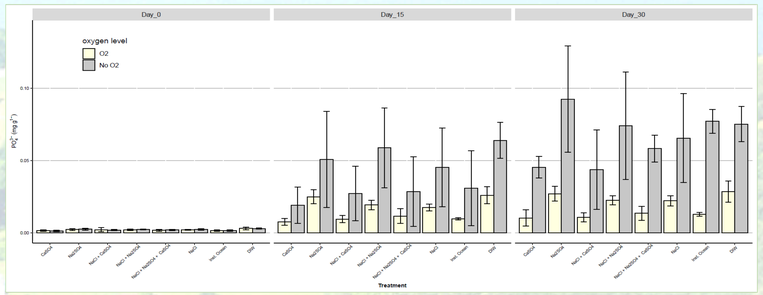

Figure 2. Concentration of bioavailable P in aerobic and anaerobic soil water with eight different saline treatments at different period of days (t=0, 15, 30). Bars represent the standard error of the mean.

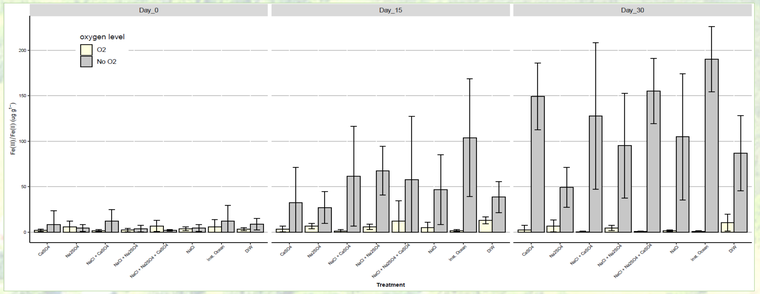

Figure 3. Concentration of extractable Fe in aerobic and anaerobic soil water with eight different saline treatments at different period of days (t=0, 15, 30). Bars represent the standard error of the mean.

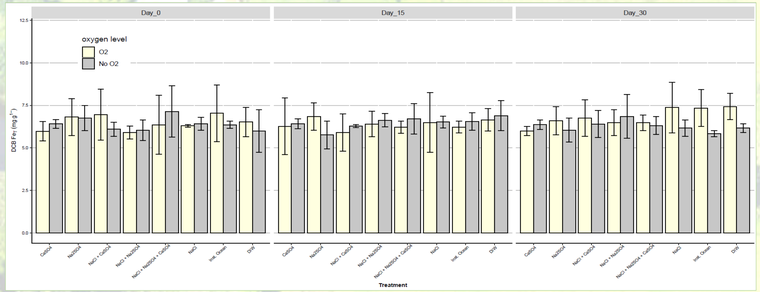

Figure 4. Mean changes of Fe concentration in treated soils across eight different saline treatments under aerobic and anaerobic conditions. Data were grouped according to soil collected days (t=0, 15, 30). Bars represent the standard error of the mean.

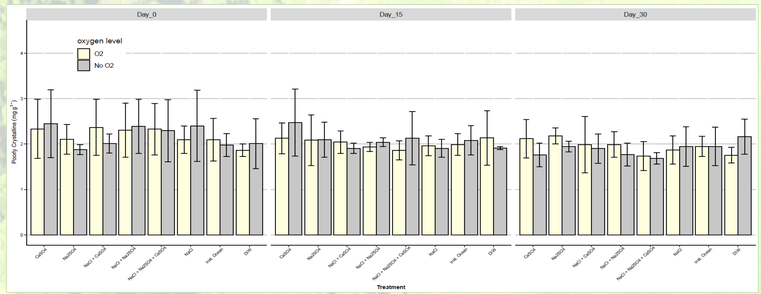

Figure 5. Mean changes of non-crystalline Fe in treated soils across eight different saline treatments under aerobic and anaerobic conditions. Data were grouped according to soil collected days (t=0, 15, 30). Bars represent the standard error of the mean.

Discussion and Conclusion

The data show that saltwater intrusion can stimulate Fe and P release under anaerobic conditions despite variation in saltwater compositions. The pattern of increasing Fe and PO_4^{3-} concentration under anaerobic conditions with increasing time in all eight salt treatments indicates that in anaerobic saline sediments Fe is less available to potentially precipitate with PO_4^{3-} (Hartzell et al. 2010). Our observation that soil-water Fe concentration declined as time changed from day 15 to day 30 under aerobic conditions suggests that Fe may be re-oxidized to Fe(III) and precipitate back with PO_4^{3-} into soils (Ann et al. 2000; Hartzell et al. 2010). Surface active ferrous compounds provide major sorption sites for P retention under anaerobic conditions (Ann et al. 2000; Patrick et al. 1974). Although anaerobic conditions in soil can increase sorption sites, the large numbers of these sites have lower bonding energy for P than do the smaller number of sites available in the aerobic soil (Ann et al. 2000; Patrick et al. 1974), inducing the P release under anaerobic condition. The result supports the mechanism in which the anaerobic layer between saltwater and soil can act as a catalyst for PO_4^{3-} release in coastal regions (Hartzell et al. 2010).

The high levels of soil-water P concentration in this study are likely the result of a combination of legacy P (Sharpley et al. 2013) and new P as farmers are still applying fertilizers to fields (Tully et al. 2019). In contrast to the Fe release trend, the soil-water P concentration was relatively high in treatments consisted of Na^+ (Fig. 2). Many studies demonstrate that P concentration in soil solution increased considerably at high sodicity (Pratt et al. 1948; Chhabra et al. 1981; Gupta et al. 1990). The high exchangeable Na^+ can increase the soil-water pH and conductivity, which shifts the solid P-solution P equilibrium in favor of maintenance of high P concentrations in aqueous solutions (Gupta et al. 1990). The result of this study reinforces the idea that soil-water P concentration correlates with sodicity.

The total soil Fe remained almost the same across the eight treatments (Fig. 4), but the poorly crystalline Fe decreased a slight amount (0.3±0.8 mg/g) from day 0 to day 30 (Fig. 5). This trend supports the finding in previous saltwater intrusion research (Tully et al. 2019). The poorly crystalline Fe tends to bind with P and forms Fe-P complexes in coastal agricultural lands through hydration (Wahid et al. 1993). Thus, soil pore-water Fe and P concentrations increase and poorly crystalline Fe in soil declines through time reinforce the mechanism that Fe mediates and P concentrations in solution. Furthermore, the P sorption potential of coastal soils can be predicted from the concentration of poorly crystalline Fe (Hogan et al. 2004). The high concentration of poorly crystalline Fe partially explains high levels of P in the selected agricultural soils (Fig. 2).

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